

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C11D 7/50, C23G 5/028	A1	(11) International Publication Number: WO 97/32001 (43) International Publication Date: 4 September 1997 (04.09.97)
(21) International Application Number: PCT/US97/03085 (22) International Filing Date: 26 February 1997 (26.02.97) (30) Priority Data: 08/609,590 1 March 1996 (01.03.96) US (71) Applicant: ALBEMARLE CORPORATION [US/US]; 451 Florida Street, Baton Rouge, LA 70801 (US). (72) Inventor: LEE, Burnell; 408 Warwick Drive, Naperville, IL 60565 (US). (74) Agents: PIPPENGER, Philip, M. et al.; Albemarle Corporation, Patent and Trademark Division, 451 Florida Street, Baton Rouge, LA 70801 (US).		(81) Designated States: CA, JP, KP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: STABILIZED BROMINATED ALKANE SOLVENT (57) Abstract A stabilized solvent composition which is comprised of: a solvent portion which includes at least 90 wt.% n-propyl bromide; and a 1,4-dioxane-free stabilizer system which includes 2,2-dialkoxypropane in which each alkoxy group independently contains up to 3 carbon atoms. The solvent composition is useful as a degreaser and cleaner in both cold and vapor cleaning systems.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

STABILIZED BROMINATED ALKANE SOLVENT

Background of the Invention:

This invention relates to a novel, high performance solvent composition based upon a brominated alkane solvent and a 1,4-dioxane-free stabilizer system.

5 The degreasing and cleaning industries are presently facing a ban on the use of 1,1,1-trichloroethane (TCE) as a deterging solvent. The ban is based upon 1,1,1-trichloroethane's relatively high ODP (Ozone Depletion Potential). Several alternatives have been suggested, but most have been rejected due to the lack of high solvent function, cost, toxicity, and flammability. One alternative, n-propyl bromide, looks to be ideal. It has a low and acceptable
10 ODP. It has been shown that its solvent function is similar to that of 1,1,1-trichloroethane and that it can be made relatively pure, say 99+ wt%, at an acceptable cost. Further, n-propyl bromide shows promise in toxicity tests. There is some confusion in the art as to its flammability, but recent testing has shown that it can be considered non-flammable.

Experimental work shows that n-propyl bromide can be used in both cold and vapor
15 cleaning systems. Surprisingly, it has been learned that n-propyl bromide is fairly stable when used at low temperatures, say temperatures up to 55° C. Tests have shown that in cold cleaning systems, n-propyl bromide needs little, if any, stabilization. However, if n-propyl bromide is used in vapor cleaning systems, then stabilization is necessary. The higher temperatures, say 69 - 71° C, can lead to the corrosion of metals such as steel, titanium, aluminum and
20 magnesium. It is believed that the metal catalyzes the dehydrobromination of n-propyl bromide to yield HBr which in turn is available to corrode the metal.

The prior art is replete with stabilizers to attenuate the catalytic activity of the metal and/or to deactivate any hydrogen halide produced. The art is most instructive in the area that was of high interest, i.e., the area concerning chlorohydrocarbon solvents. Much less art is
25 available in the area of bromohydrocarbon solvents. Due to the newly discovered attractiveness of brominated solvents, the art is just now vigorously investigating the selection of the best combination of brominated solvent and stabilizing system. The combination possibilities are innumerable, but the advantage will go to the discoverer of that ideal match between a particular brominated solvent and a particular stabilizing system. Not all of the old prior art solvent

system components are now considered to be acceptable candidates due to present day concerns about health and the environment. For example, a very common and efficacious stabilizing component, 1,4-dioxane, is not now favored due to health concerns. This is unfortunate, because 1,4-dioxane is an especially good stabilizer component for attenuating an increase
5 in the acidity of a solvent system under strong oxidizing conditions.

It is, therefore, an object of this invention to provide a degreasing and cleaning solvent which is highly efficacious and which is friendly to both the user and the environment.

The Invention:

This invention relates to a stabilized degreasing and cleaning solvent composition which
10 is comprised of: a solvent portion which includes at least 90 wt% n-propyl bromide; and a 1,4-dioxane-free stabilizer system which comprises 2,2-dialkoxyp propane. In addition, the stabilizer system may contain nitroalkane, nitrobenzene, an epoxide, such as 1,2-butylene oxide and/or an amine. Except as indicated to be otherwise, the wt% and ppm values used herein are based upon the total weight of the solvent composition.

15 Preferably, the n-propyl bromide is supplied to the composition as 99+ wt% n-propyl bromide, with the most common impurity being iso-propyl bromide. The weight percentage and ppm recited in this paragraph are based on the total weight of n-propyl bromide and impurities. Commercially suitable n-propyl bromide may be accompanied by as much as 6 wt% iso-propyl bromide. n-Propyl bromide of much less purity is permissible, but not desired.
20 The iso-propyl bromide impurity is naturally found in the raw n-propyl bromide product, but its presence can be attenuated by distillation. It is not a benign impurity as it is very much less stable than n-propyl bromide and, thus, can result in aggressive corrosion. A typical raw n-propyl bromide product will contain 96 wt% n-propyl bromide and 4 wt% iso-propyl bromide. For vapor degreasing and cleaning, the preferred iso-propyl bromide content will be kept low,
25 say within the range of from 250 to 1000 ppm. n-Propyl bromide can be purchased commercially from Albemarle Corporation, Richmond Virginia.

The solvent composition is, as before noted, 1,4-dioxane-free--that is, it comprises no more than an impurity amount of the solvent composition, say less than 500 ppm. It is preferred that no 1,4-dioxane whatsoever be present in the solvent composition.

The 2,2-dialkoxypropane component of the stabilizer system is characterized in that the alkoxy groups can each independently contain one to three carbon atoms. For example, each alkoxy group can be selected from methoxy, ethoxy and propoxy. The most preferred 2,2-dialkoxypropane is 2,2-dimethoxypropane, which is a known compound and has been
5 given CAS #77-76-9. The dialkoxypropanes of this invention have been discovered to have an unusual ability for attenuating the acid content of n-propyl bromide based solvent compositions which are under oxidation stress. Other stabilizer compounds, such as 1,3-dioxolane, acetal, diethoxymethane and acetaldehyde dimethyl acetal, are not nearly as effective.

10 The 2,2-dialkoxypropane is generally used in an amount within the range of from 2.0 to 6.0 wt%, based upon the total weight of the solvent composition. Preferred is 2.0 to 4.0 wt%.

As before noted, the stabilizer system of this invention can additionally contain conventional stabilizers, e.g., nitroalkane, nitrobenzene, epoxide and/or amine. These additional
15 stabilizers act to further enhance the stability of the solvent system so that the dehydrobromination catalyzed by the metal is discouraged and/or so that HBr which is produced is neutralized.

The nitroalkanes usable in the present invention include nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane and nitrobenzene. They are usable either singly or in the
20 form of a mixture of two or more of them. The nitroalkane is preferably nitromethane, nitroethane or mixtures thereof. The most preferred is nitromethane. The amount of nitroalkane used will generally be within the range of from 0.045 to 1.0 wt%. A preferred amount will be within the range of from 0.3 to 0.6 wt%.

The epoxides include epichlorohydrin, propylene oxide, butylene oxide, cyclohexene
25 oxide, glycidyl methyl ether, glycidyl methacrylate, pentene oxide, cyclopentene oxide and cyclohexene oxide. Preferred is 1,2-epoxybutane. They are usable either singularly or in the form of a mixture of two or more of them. The amount of epoxide used will generally be within the range of from 0.045 to 1.0 wt%. A preferred amount will be within the range of from 0.3 to 0.6 wt%.

The amines include hexylamine, octylamine, 2-ethylhexylamine, dodecyl-amine, ethylbutylamine, hexylmethylamine, butyloctylamine, dibutylamine, octadecyl-methylamine, triethylamine, tributylamine, diethyloctylamine, tetradecyldimethylamine, diisobutylamine, diisopropylamine, pentylamine, N-methylmorpholine, iso-propylamine, cyclohexylamine, butylamine, isobutylamine, dipropylamine, 2,2,2,6-tetramethylpiperidine, N,N-di-allyl-p-phenylenediamine, diallylamine, aniline, ethylenediamine, propylenediamine, diethylene-triamine, tetraethylenepentamine, benzylamine, dibenzylamine, diphenylamine and diethyl-hydroxyamine. They are usable either singularly or in the form of a mixture of two or more of them. The amount of amine used will generally be within the range of from 0.25 to 1.0 wt%. A preferred amount will be within the range of from 0.3 to 1.0 wt%.

It is within the scope of this invention for the solvent compositions of this invention to be used in the presence of and in conjunction with other solvents or solvent systems and additives. For example, the solvent compositions of this invention can be mixed with a solvent such as hexane, or n-butyl bromide. An exemplary additive is an anti-rust additive. The solvent composition of this invention may comprise from less than 50 to more than 90 wt% of the total weight of the solvent composition of this invention and the other solvent or solvent system or additive.

Quantitatively, the solvent compositions of this invention, as before noted, will contain at least 90 wt% n-propyl bromide, with the balance being impurities, e.g., iso-propyl bromide, the stabilizer system of this invention and any other additives desired by the practitioner. A typical solvent composition in which the n-propyl bromide used is not particularly pure, will contain 90 - 92 wt% n-propyl bromide, 4 - 6 wt% iso-propyl bromide, 0.25 - 1.0 wt% nitromethane, 0.25 - 1.0 wt% 1,2-butylene oxide and 2.0 - 6.0 wt% 2,2-dialkoxypropane, e.g., 2,2-dimethoxypropane. If the n-propyl oxide is of high purity, then the n-propyl bromide could be 94 - 98 wt% of the solvent composition, all based on the total weight of the solvent composition.

The solvent compositions of this invention are suitable for use in cold cleaning applications and in vapor cleaning operations. The former are generally characterized by immersion of the article to be cleaned in the solvent composition at a temperature which is usually within the range of from room temperature to 55° C. Vapor cleaning is characterized

by passing the article to be cleaned through a vapor of the solvent composition, with the article at a temperature which causes condensation of the vapor on its surfaces. The condensate effects its cleaning function and then drips off. The vapor temperatures are generally approximate to the boiling point of the solvent composition, which, in the instant case, will be around 65
5 to 75° C depending upon the particular quantitative and qualitative identity of the solvent composition being used. For a solvent composition where the n-propyl bromide content is very high, say above 95 wt%, the boiling point will be around 69 - 72° C.

The following illustrates the efficacious nature of solvent compositions of this invention. It is not intended for the Example to be taken, in any way, as limiting the scope of the
10 inventions described herein.

EXAMPLE

A solvent composition was prepared by mixing the following ingredients together:

96.5 wt% n-propyl bromide
2.5 wt% 2,2-dimethoxypropane
15 0.5 wt% 1,2-butylene oxide
0.5 wt% nitromethane

The acidity of the composition was determined. Subsequently, the composition was exposed to oxidation stress in the presence of steel strips as described in Military Specification MIL-T-81533A Notice I, 29 October 1991, "Trichloroethane 1,1,1, (Methyl Chloroform)
20 Inhibited, Vapor Degreasing". See in particular, Paragraph 4.4.7.2, entitled "Acidity after accelerated oxidation".

The determination of the acidity was done in accordance with Paragraph 4.4.71 of the same Specification.

In accordance with the directions in Paragraph 4.4.7.2, an apparatus was set up as shown
25 in Figure 1 of the Specification. A strip of steel, 1/2 inch by 2 inches by 1/16 inch, was suspended by means of an uncoated cooper wire so as to remain above the liquid level in the flask. Another steel strip, 1/4 inch by 3/4 inch by 1/16 inch, was placed in the bottom of the flask. The strips conformed to SAE steel within the range of 1010 and 1040. The condenser water was turned on. The oxygen flow was started and regulated to 10 - 12 bubbles per minute.
30 The solution was then heated to reflux for a period of 48 hours. After the 48-hour period, the

solvent was cooled to ambient temperature. A 25 ml sample was taken and its acidity determined, again, in accordance with Paragraph 4.4.7.1.

This same procedure was repeated with different compositions--the only difference being the presence of a different stabilizer which was used in the stead of 2,2-dimethoxypropane. This other stabilizer is identified in the Table below. The n-propyl bromide and the nitromethane and 1,2-butylene oxide co-stabilizers were used in the same amounts in all cases

TABLE

	STABILIZER	BEFORE/AFTER TEST	ACIDITY PPM AS HCL
10	1,4-dioxane	before	2.0
	1,4-dioxane	after	21.8
	1,3-dioxolane	before	29.0
	1,3-dioxolane	after	65.7
	diethoxymethane	before	33.1
15	diethoxymethane	after	124.0
	2,2-dimethoxypropane	before	30.7
	2,2-dimethoxypropane	after	46.3
	acetaldehyde dimethyl acetal	before	34.9
	acetaldehyde dimethyl acetal	after	92.5
20	acetaldehyde dimethyl acetal	before	39.3
	acetaldehyde dimethyl acetal	after	96.9

CLAIMS

1. A stabilized solvent composition which is comprised of: a solvent portion which includes at least 90 wt% n-propyl bromide; and a 1,4-dioxane-free stabilizer system portion which comprises 2,2-dialkoxypropane in which each alkoxy group independently contains
5 up to 3 carbon atoms.
2. The solvent composition of claim 1 wherein the n-propyl bromide is present in the solvent composition in an amount within the range of from 94 to 98 wt%.
3. The solvent composition of claim 1 the 2,2-alkoxypropane is 2,2-dimethoxypropane.
- 10 4. The solvent composition of claim 1 wherein the stabilizer system additionally contains nitroalkane, epoxide and/or amine.
5. The solvent composition of claim 4 wherein there is 2.0 - 6.0 wt% 2,2-dialkoxypropane, and at least one of the group consisting of 0.045 - 1.0 wt% nitroalkane, 0.045 - 1.0 wt% epoxide, 0.045 - 1.0 wt% amine.
- 15 6. The solvent composition of claim 5 wherein there is 2.0 - 6.0 wt% 2,2-dimethoxypropane, and at least one of the group consisting of 0.045 - 1.0 wt% nitromethane, 0.045 - 1.0 wt% 1,2-butylene oxide, and 0.045 - 1.0 wt% amine.
7. A process for cleaning an article which comprises immersing the article in a solvent composition comprised of a solvent portion which includes at least 90 wt% n-propyl
20 bromide; and a 1,4-dioxane-free stabilizer system portion which includes 2,2-dialkoxypropane in which each alkoxy group independently contains up to 3 carbon atoms, said solvent composition being at a temperature within the range of from room temperature to 55° C.
8. A process for cleaning an article which comprises exposing the article to the vapor emanating from a boiling body of a solvent composition comprised of a solvent portion
25 which includes at least 90 wt% n-propyl bromide; and a 1,4-dioxane-free stabilizer system portion which includes 2,2-dialkoxypropane in which each alkoxy group independently contains up to 3 carbon atoms.

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 97/03085

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C11D7/50 C23G5/028

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D C23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 609 004 A (DIPSOL CHEMICAL CO LTD) 3 August 1994 see claims 6-12; table 1 ---	1-7
A	DATABASE WPI Section Ch, Week 9532 Derwent Publications Ltd., London, GB; Class D24, AN 95-243891 XP002034755 & JP 07 150 196 A (DIPSOL KK) , 13 June 1995 see abstract ---	1-7
P,A	DE 196 14 355 A (TOSOH CORP) 31 October 1996 see the whole document --- -/--	1-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

9 July 1997

Date of mailing of the international search report

22.07.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 97/03085

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	<p>DATABASE WPI Section Ch, Week 9620 Derwent Publications Ltd., London, GB; Class B05, AN 96-196546 XP002034753 & JP 08 067 643 A (TOA GOSEI CHEM IND LTD) , 12 March 1996 see abstract</p> <p>-----</p>	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/03085

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0609004 A	03-08-94	JP 2576933 B	29-01-97
		JP 6220494 A	09-08-94
		DE 69402222 D	30-04-97
		ES 2099539 T	16-05-97
		US 5492645 A	20-02-96

DE 19614355 A	31-10-96	FR 2732963 A	18-10-96
		JP 8337795 A	24-12-96
